

NMR Imaging of Heterogeneous Coal Macromolecular Networks

George D. Cody, David C. French and Robert E. Botto

Chemistry Division, Argonne National Laboratory, 9700 So. Cass Ave.
Argonne, IL 60439

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Introduction

Over the past few years, we have been developing new NMR imaging strategies for probing the chemical and physical structure of coal. Early experiments focused on proton NMR imaging techniques for spatially resolving individual macerals within a solid coal specimen.¹ Distinction of individual macerals was achieved by taking advantage of differences in proton density or in spin-lattice relaxation rates, which were shown to vary significantly between the two maceral types. With the implementation of multipulse proton line narrowing in the presence of large static magnetic field gradients, together with back-projection reconstruction NMR imaging methods², we were able to image and distinguish macroscopic resinite and vitrinite regions within a 2-mm \times 2-mm \times 1.4-mm specimen of Utah Blind Canyon (APCS No. 6) coal to an in-plane resolution of about 150 μ m.

More recent efforts have focused on obtaining information concerning solvent accessibility in coals and maceral domains by proton NMR imaging of mobile proton distributions resulting from solvent swelling.³ Imaging in the presence of deuterated solvents illuminated proton distributions of mobile phases within the coal macromolecular structure preferentially. Images with resolutions of 40 to 80 μ m were obtained using protic solvents, and showed the presence of different macerals, mineral cleats, and microfractures. Regions which differed with regard to pyridine accessibility were also contrasted in the images. We also were prompted by the initial investigation to elucidate the details of transport behavior of pyridine into coal during swelling. In that study,⁴ time-resolved proton NMR images of pyridine penetrating a homogeneous sample of high volatile bituminous A rank vitrain (APCS No. 4) that had been pre-extracted with pyridine were used to describe the uptake behavior. In addition to coal swelling in pyridine, we investigated transient state imaging results from three polymer-solvent systems for comparison: polyethylmethacrylate swollen in methanol, polymethylsilicone swollen in hexafluorobenzene, and isobutyl rubber swollen in toluene. A model for case II transport in coals was described.

The purpose of this presentation is to review these earlier studies and to provide an overview of the present and future applications of NMR imaging for coal structure determination.

Results and Discussion

Solvent Swelling Studies.

Since the early work of Sanada and Honda, solvent swelling has been employed to probe the physical structure of coal.⁵ The swelling behavior of bituminous coals in solvents such as pyridine has been used to assess different strengths or types of secondary interactions which determine the macromolecular structure of coal.⁵⁻⁹ These include weak interactions of less than ~ 15 kcal mol⁻¹, such as hydrogen bonding, van der Waals interactions, weak complexes, and π -electron intermolecular interactions.¹⁰⁻¹² The secondary interactions which can be broken by one solvent may be unaffected by a different solvent. A high degree of secondary interactions imparts rigidity to the macromolecular structure in coals, whereas disruption of these secondary interactions by a good swelling solvent mobilizes the structure. Pyridine has been found to effectively relax all of the secondary interactions in coal, leaving only covalent bonds intact.^{10,11} It is known that the chemical heterogeneity of coal leads to anisotropic swelling.¹² Coal swelling has been found to be greater perpendicular to the bedding plane than parallel to it.¹³ Cracking at mineral-organic interfaces is also expected due to differential swelling of the organic matrix relative to mineral matter.

Important information concerning solvent accessibility to the pore structure and maceral domains in coals also may be obtained by imaging mobile proton distributions resulting from solvent swelling. Images of coals swollen with perdeuterated solvents can be used to map mobile phases in the coal macromolecular structure, while images obtained with protic solvents map distributions of the ingressed solvent.

Here, we discuss the results from two different three-dimensional (3D) NMR imaging techniques for spatially mapping mobile proton distributions in coals that have been swollen with pyridine-*d*₅ or pyridine. Three-dimensional back-projection techniques

employing a 3D Radon transform inversion reconstruction algorithm were used to map mobile proton distributions on the basis of T_1 (spin-lattice relaxation time) differences. Contrast based on differences in T_2 (spin-spin relaxation time) was achieved employing 3D gradient recalled echo (GRE) pulse sequence for data acquisition, and image reconstruction by 3D Fourier transform (FT). Both techniques display proton distributions of mobile phases within the solid preferentially. Images with resolutions of 40 to 80 microns show the presence of different macerals, mineral cleats, microfractures, and the distribution of mobile macromolecular phases in solvent swollen coals. Regions which differ with regard to pyridine accessibility are also contrasted in the images.

The proton NMR spectrum of a specimen of Utah Blind Canyon coal swollen with pyridine- d_5 showed three distinct proton resonances. There was a broad resonance (ca. 27 kHz) arising from rigid protons, and there were two considerably narrower resonance lines discernable as aromatic and aliphatic signals arising from protons in environments of high molecular mobility. Analysis of the broad and narrow components revealed that 14% of the protons are found in regions of high mobility. The fraction aromaticity of mobile phase protons calculated from line simulation was 0.45 compared to a value of 0.24, obtained from proton CRAMPS analysis of the dried coal. The estimated contribution to the total proton signal from residual protons in the pyridine- d_5 was less than 0.1%, while the observed f_a^H increased nearly two-fold as a result of swelling. Clearly, there is a substantial enhancement in the amount of motionally narrowed aromatic proton signal due to swelling.

The 3D surface-rendered NMR image of the Utah coal swollen with pyridine- d_5 was a good representation of the general topology of the actual specimen. For example, a dark feature was found which is known to be a macroscopic crack from solvent swelling the coal. Other dark features on the surface were derived from regions where rigid macromolecular proton signal is suppressed by employing a short relaxation delay; the magnetization of the rigid phase is saturated due to the longer T_1 of these protons.

An 80-micron thin section (slice) through the 3D radon reconstruction showed image contrast from the same sources affecting the 3D surface-rendering. Mobile proton phases resulting from relaxation of the secondary interactions in the coal by swelling with pyridine- d_5 appear bright. Void spaces or mineral deposits which lack protons appear dark. In addition to regions of low proton density, regions of the rigid macromolecular network with long T_1 's in the coal appear dark due to the T_1 saturation effects.

The 1H single-pulse NMR spectrum of pyridine-swollen Lewiston-Stockton coal exhibited a single resonance from the pyridine protons exclusively, whose linewidth was 424 Hz. The 1H linewidth of pyridine in the Utah coal was 340 Hz. The T_1 of pyridine protons in both samples was measured by progressive saturation, and a value of approximately 1.3 ms was obtained. The baseline-to-baseline projection width of the Lewiston-Stockton coal recorded with the GRE pulse sequence and the phase-encoding gradients off was 11.2 kHz, and that of the Utah coal was 13.5 kHz. The pyridine natural linewidths and baseline-to-baseline projection widths, along with the 1mm³ specimen sizes, afforded an in-plane resolution of 50 and 40 microns, respectively, for the two coals.

The 3D surface-rendered GRE images of the Utah and Lewiston-Stockton pyridine swollen coals exhibited bright features resulting from regions in the coals which contain a high density of mobile pyridine; dark areas resulted from regions which are inaccessible to the solvent. Photographs of the Utah and Lewiston-Stockton coal showed a close correspondence between the shape of the coal specimens and the surface-rendered GRE image geometries. Also, features devoid of pyridine such as pits, cracks, and gouges appeared magnified in the images. The vertical feature on the front face of the 3D surface-rendering of the Lewiston-Stockton specimen showed a microscopic structure contiguous with the surface of the specimen which is inaccessible to pyridine. The photograph showed that this is a solid region in the coal rather than a void space.

Slices of the interior of the Lewiston-Stockton coal show the presence of contrasting horizontal bands in the *xy*-plane similar to the lamellar structures visible in the photograph of the coal. A dark vertical feature was seen which corresponds to the same region which appears as a void in the 3D surface-rendering, and indicated that this interior structure runs through the object to its surface. Since the photograph shows that this area of the specimen is solid, the dark structure in the images is clearly a region of low pyridine accessibility rather than a void space. When the coal was swollen with pyridine, the secondary interactions binding strata within the specimen were relaxed. Contrasting bands in the images showed that differential swelling in the bedding plane has produced microfractures and regions with greater or lesser pyridine accessibility.

This preliminary investigation has shown that 3D NMR imaging is a promising tool for studying solvent swelling of coals. This non-destructive technique revealed rich microscopic detail concerning the penetration and accessibility of a solvent into the interior of coal specimens. Further development of this technique also presents the possibility for visualization and analysis of the dynamics of the coal swelling process which can be used to elucidate coal physical structure. In addition, several preparatory pulse sequences prior to the imaging experiment may be employed for the quantitative characterization of NMR relaxation phenomena and solvent diffusion in coals. Image contrast produced by differences in the mobility of the macromolecular network in the coal will be compared with image contrast produced by differences in solvent accessibility in the same specimen. Coal

specimens with known petrography will be utilized and correlated with NMR images obtained using multiple-pulse proton decoupling methods prior to the solvent swelling measurements.

Solvent Transport Studies

Significant insight into the character of solvent transport has been obtained through time-resolved, direct imaging of concentration gradients during solvent uptake. Early on, optical microscopic methods revealed that solvent transport in some macromolecular networks did not conform to Fickian kinetics.¹⁴ Specifically, these systems exhibited steep-gradient solvent fronts which propagate into a sample at a constant velocity, much like a shock wave; such behavior has been called case II transport to distinguish it from Fickian transport.

Case II transport is not restricted to synthetic polymers. Biopolymers and geopolymers such as cellulose and bituminous coals, for example, also exhibit case II transport behavior under suitable conditions.^{10,14,15} All that is required for case II transport is that the dry network exist initially in a glassy state and that the penetrating solvent is capable of suppressing T_g .

Given the interesting physical behavior of glassy networks near their glass transition, the search for a theoretical basis for non-Fickian behavior has been irresistible for both experimentalists and theorists. To date, numerous theories abound.¹⁶⁻²⁴ While the specific approaches to this problem vary from one model to another, universally they rely on the generality that case II behavior results from coupled solvent diffusion and network relaxation.^{25,26} There are several rigorous approaches which quantify case II transport in terms of a relatively small set of physically based dynamic parameters.¹⁹⁻²⁴ These models tend to be valid only for very small displacements from equilibrium, because linear behavior of the governing equations is required in order to obtain an analytical solution. Large scale departures from equilibrium conditions requires that the concentration dependence on each of the dynamic parameters be considered explicitly. This has resulted in a complicated data analysis, stemming from a many-fold expansion of the parameter set and, consequently, an increase in the total number of degrees of freedom of the model.

Many, if not most, applications involving solvent-macromolecular systems are far from equilibrium. In the present paper, the essential characteristics of case II transport are exploited for the purpose of reducing the dynamic parameter set size, in order to simplify quantification under conditions far from equilibrium, e.g., the situation of solvent transport following immersion of a dry macromolecular network into a solvent reservoir. Case II transport of methanol in polyethylmethacrylate (PEMA) and pyridine in coal is explored and compared with Fickian transport of toluene in polybutadiene rubber (PBD) and hexafluorobenzene in polymethylsilicone (PMS) using magnetic resonance microscopy and optical microscopy.

The characteristic relaxation times for each solvent-network system were established at full dilation using a standard inversion-recovery pulse sequence to derive T_1 , and a Hahn spin-echo pulse sequence to derive T_2 . It is acknowledged that in protonated solvent systems, contributions to the signal intensity can arise from both the protons in the solvent and protons associated with the mobile network. Analysis of the NMR spectral and dynamic characteristics of these swollen networks in deuterated solvents reveals that, in general, only a minor contribution to the total signal intensity results from the mobile network protons. This contribution is significant, however, in the case of PBD in toluene. No signal is detectable from the rigidly bound protons in the glassy regions of PEMA or coal due to severe dipolar broadening (linewidth > 20 kHz) in the rigid solid. Obviously, in the case of ^{19}F imaging of solvent transport into polymethylsilicone, signal is derived from the solvent exclusively.

In the present experiments, two-dimensional (2D) images are sufficient to elucidate the fundamental aspects of the transport phenomena. In order to ensure that the transport process was also two dimensional, the upper and lower sample surfaces were protected from solvent infiltration by glass cover slips which restricted the flow of solvent to cross only the exposed faces of each sample. Each sample is rectangular with initial dimensions on the order of $1.2 \times 1.2 \times 1$ mm. The experimental protocol involved immersing the sample in the solvent for a period of time, removing it from the solvent bath, acquiring an image, and re-immersing it. During the imaging stage the sample was placed in cell with "plugs" such that the free volume within the cell was minimized. It was anticipated that this would reduce the amount of desorption over the duration of the imaging.

In order to obtain sufficiently high quality images, given the dynamic behavior of the three protonated solvent/macromolecule systems, it was necessary to acquire 24 (128 point) transients with a recycle delay of 200 ms for each of 128 phase-encoded gradient positions using a standard imaging spin-echo pulse sequence.²⁷ This yielded reasonably high quality 2D images, with a resolution on the order of 70 μm , which was obtained over intervals of approximately 10 min. Typically a 64-kHz spectral width was chosen, establishing an echo time on the order of 0.5 ms. In the case of ^{19}F imaging, a longer T_1 and an inherently lower sensitivity of the nucleus necessitated the acquisition of 32 scans per phase encoded position and a recycle delay of 500 ms; this resulted in a time interval on the order of 30 min to obtain a quality image. It is clear that during the time that the images are acquired some

spatial averaging does take place. However, in all cases, the entire uptake process takes between 3 to 4 hrs, and therefore, it is assumed that the averaging is relatively minor.

A 2D ^{19}F image projection of a specimen of polymethylsilicone swelling in hexafluorobenzene, observed at some intermediate time, exhibited a shallow concentration gradient into the core of the specimen. The 2D image of polyethylmethacrylate in methanol was strikingly different; in this case a sharp front was observed with a nearly constant solvent concentration behind the front.

Magnetic resonance imaging data in the form of 1D slices, reconstructed from the center of the 2D image projections, revealed sequential cross-sections through PBD dilated in toluene; a sizable contribution to the image intensity arose from the protons associated with the rubbery PBD itself. Superimposed on this was the additional signal due to the solvent. Clearly evident, however, were the smooth, exponential, solvent gradients directed into the core of the sample, indicating a Fickian transport mechanism. Fickian transport was also revealed in the case of the fluorinated solvent in PMS. Smooth solvent gradients were clearly evident despite the lower signal-to-noise ratios obtained in the ^{19}F images.

The character of transport was drastically different for PEMA swollen in methanol. The presence of a sharp solvent front and solvent absent core clearly indicated case II transport. This behavior is typical of many acrylate polymers swollen in a variety of solvents, and it has been detected previously by NMR imaging techniques.²⁸⁻³⁰ The imaging results gave some indication of a sigmoidal solvent front similar to that derived numerically, and suggested that the NMR images might be used to help constrain values of the solvent activity. Pyridine transport in coal also exhibited case II behavior, whose signature was revealed by sharp solvent fronts moving into the sample. The situation was complicated by the formation of a crack on the left side of the lower most cross-section, which destroyed the symmetry of the solvent fronts. The formation of cracks accompanying case II transport is not unusual, nor unexpected, considering the magnitude of the strain gradients along the solvent front.

The measured front velocities were constant for both the PEMA and the bituminous coal, consistent with case II transport. There was some concern that a degree of spatial uncertainty or blurring may occur during evolution of the front within the imaging interval, leading to an apparent reduction in the gradient of the solvent front. Furthermore, distortions in image intensity due to T_2 effects were expected to add some further degree of uncertainty. The accuracy of the magnitudes of the front velocities derived from magnetic resonance imaging, however, are not subject to these effects. Hence, the velocities provide a valuable and quantitative constraint for the parameterization of the uptake data.

Direct measurement of linear dilation accompanying swelling is a simple means to quantify the overall swelling behavior of rubbery networks.^{31,32} Linear dilation behavior for PBD and PMS were consistent with Fickian transport in rubbery networks. Given the uptake data, it was trivial to derive a mass-fixed diffusion coefficient through linear fitting of the experimental data. The generation of a curve for Fickian transport, in the present case, requires solving the two-dimensional diffusion equation and integrating this solution with respect to time. Fitting of the dilation data results in values of $D_R = 2.5 \times 10^{-6} \text{ cm}^2/\text{s}$ and $1.1 \times 10^{-6} \text{ cm}^2/\text{s}$ for PBD-toluene and PMS-hexafluorobenzene, respectively. These relatively large values of D_R reflect the high degree of inter- and intra-molecular mobility of these networks, which explains the rapidity with which the rubbery systems respond to applied stresses that are osmotic in nature.

In the case of solvent transport in systems undergoing a glass transition, or case II transport, we have defined the uptake behavior using three parameters: a characteristic cooperative diffusion coefficient, D_c , governing dilation of the network; a molecular relaxation rate constant, β , which is given by the relationship $\beta = K_{og}/\eta_1$, where η_1 is the bulk viscosity and K_{os} is the osmotic modulus; and a critical solvent concentration, C^* , above which there is a transformation of the network from a glass to a rubber. However, there are several degrees of freedom associated with the present model of case II transport. Without constraints on the magnitude of C^* or β , it is not possible to uniquely define the three transport parameters. In the present case the dilation data for both PEMA and bituminous coal were fitted to characteristic case II curves, using β as a floating variable while C^* was independently constrained. The final constraint used was the solvent front velocity, v , obtained from magnetic resonance imaging.

A relationship between C^* and solvent concentration was established by relating the change in free volume of the solvent-polymer system to contributions from the respective free volumes of polymer and solvent taken independently. Essentially linear T_g suppression with concentration is observed at low solvent concentrations, $\Delta T = -kC_S$, where $\Delta T = T_{g,\text{supp}} - T_{g,\text{dry}}$, k is typically in the range of 200 - 500 °K for a variety of solvents, and C_S is the volume fraction of the solvent. Recalling that T_g of PEMA is only 308 °K, the value of C_S , accordingly, is anticipated to be very small. Using a lower value of k , we calculate $C_S = 0.05$, yielding $C^* = 0.17$. Bituminous coal is reported to have its T_g on the order of 650 to 700 °K, suggesting that C_S of pyridine must be very high. Indeed, calculations along these lines have indicated that C_S (calculated) actually exceeds the equilibrium C_S associated with coal dilated at room temperature at a solvent activity of 1.0.³³ On the basis of this analysis, it would appear that pyridine is not capable of suppressing coal's T_g to less than room temperature, which is inconsistent with the present results. Recent experimental results derived from incremental solvent sorption isotherm experiments on bituminous coal,

however, clearly indicate the presence of a glass transition at solvent activities less than 1.0, yielding a magnitude of C^* on the order of 0.65.³⁴

The gross dilation behavior of both samples was clearly case II with an unambiguous sigmoidal uptake profile. The essential character of the present model for case II transport processes is revealed when comparing the swelling kinetics of these two glassy networks. Both samples are essentially the same size, with uptake occurring over essentially the same interval of time. The glassy diffusion coefficients for the two samples are also very similar in magnitude. The coal's network relaxation rate following the glass transition, however, is almost 15 times larger than that of PEMA. It is the relative magnitudes of the critical concentration parameter, C^* , which compensates for this disparity in the relaxation dynamics and results in comparable overall uptake times. For the case of PEMA swollen in methanol, C^* is relatively small. In the present model, network relaxation at the glass transition drives diffusion; all other things remaining equal, the sooner relaxation occurs the faster transport evolves.

Comparing all four samples, the nearly two order of magnitude difference in diffusion coefficients between the Fickian and case II systems is compensated by the lack of any phase-transition induced, network relaxation in the Fickian systems. Generally, these results confirm assertions made by authors of one of the earliest papers on the applications of magnetic resonance imaging to diffusion in glassy polymers;²⁸ i.e., it is the presence of the phase transition which drives the overall diffusion process.

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